

## TIME OF REMEDIATION ESTIMATES

### Enhanced Bioremediation at ST012

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#### Summary

The attached memorandum describes a screening level evaluation of enhanced bioremediation (EBR) applied to NAPL source zone targets at ST012. The purpose of the effort is to estimate timeframes for completing the remediation. The model is based on a mass balance for the NAPL source zones. Contaminants dissolve out of the NAPL into surrounding groundwater and then undergo biological degradation. Remediation is complete when contaminant fractions in the NAPL are reduced to levels that no longer impact groundwater above cleanup goals. The duration to attain this goal is known as the time of remediation (TOR). The evaluation assumes a range of initial conditions. Sulfate reduction was selected as the bioremediation process to be enhanced with the underlying assumption that the addition of sulfate will accelerate the degradation of contaminants.

Detailed numerical calculations for monitored natural attenuation before and following a hypothetical application of SEE were performed previously using the SEAM3D Model as reported in Appendix M of the TEE Pilot Test Evaluation Report (BEM, 2011). Those calculations were very complex; however, model parameters were calibrated to field data. Depletion of individual NAPL source zones can be estimated to the same order-of-magnitude with straightforward mass balances that include the same mechanisms of remediation averaged over each target soil volume. Details of the volume-averaged model are provided in Appendix B of the memorandum. The model includes mass transfer limitations on the dissolution of components from NAPL. Biodegradation was modeled with two different approaches: first order degradation and Monod kinetics including biomass growth.

Times of remediation (TOR) for untreated NAPL targets using EBR were first calculated assuming an empirical first order decay constant for degradation and a site-specific mass transfer coefficient for NAPL measured in previous studies ( $0.05 \text{ d}^{-1}$ ). Very little site data exists to support the selection of a generic decay rate constant and the value is not expected to remain constant over time. Using the rate constant cited by Amec ( $0.0125 \text{ d}^{-1}$ ) in Work Plan submittals, the calculated TOR ranged from 10 to 20 years in the Upper Water Bearing Zone (UWBZ) and 10 to 30 years in the Lower Saturated Zone (LSZ). This degradation rate constant is unsubstantiated, particularly for the UWBZ where a pilot test was not performed, and therefore these time estimates are unsubstantiated. Sensitivity calculations indicate increasing and decreasing the decay constant by a factor of ten increases and decreases the TOR by a factor of four, respectively.

**Commented [DE1]:** Maybe this is obvious, but should you also state that Amec's NAPL mass estimates were used in these calculations?

**Commented [WU2]:** Probably need a sentence or two more clearly describing the difference between the two approaches – e.g., Monod takes into account growth rate of the microorganisms, and etc. That is, explain why, as is written below, that *Monod kinetics are more comprehensive*. Help the nontechnical/nonexpert reader to understand why two approaches are used, and how the different approaches can be interpreted in terms of site understanding and decisions. All in one or two sentences, of course. ☺

**Commented [DE3]:** How does this rate compare to other literature values?

**Commented [DE4]:** Dan didn't think the rates calculated for the LSZ from the pilot test that was done were reliable

DFP says: I didn't think the rates were good for several reasons – one of which is they only used a small fraction of the data they got from the pilot study to calculate rates, because using the rest of the data would have dramatically changed their conclusions about rates.

**Commented [DE5]:** Should these be changed around, increasing the decay constant decreases the TOR?

Modeling was then performed for NAPL depletion with more comprehensive Monod kinetics for degradation using the site-specific, calibrated parameters from the SEAM3D modeling effort (BEM, 2011). These same parameters are cited in the ST012 Work Plan (Amec, 2014). The calculated TOR with Monod kinetics ranged from 90 to 140 years in the Upper Water Bearing Zone (UWBZ) and 8 to 23 years in the Lower Saturated Zone (LSZ). These estimates are based on site measured properties and calibration to site conditions. Sensitivity calculations indicate increasing the mass transfer coefficient by a factor of ten yields a slight decrease in the TOR suggesting the groundwater is near equilibrium. An order-of-magnitude decrease in the mass transfer coefficient increased the TOR in the LSZ by a factor of four but yielded a marginal increase in the TOR in the UWBZ suggesting degradation is the limiting process.

Based on the model and underlying assumptions, the concentration of sulfate reducing bacteria grew to a stationary phase concentration around 3 to 3.5 mg/L in both zones, when growth occurred. The growth period was approximately 12 to 24 months in the LSZ. The growth period in the UWBZ was on the order of 35 to 40 years assuming a zero death rate. The UWBZ growth was slow and the results were very sensitive to the death rate as a result of the low utilization rate. The calculated TOR was not strongly influenced by the assumed initial biomass concentration (0.01 mg/L). In addition, initial sulfate concentrations exceeding 8,000 mg/L provided no improvement in the TOR.

**Commented [DE6]:** Does this still use the rate constant that Amec used?

**Commented [WU7]:** Maybe I'm reading this wrong, but are we saying here that AMEC's assumption of instantaneous equilibrium (between LNAPL and GW) is actually reasonable (or at least not invalidating for the use of the model) – because biodegradation is the limiting process, not mass transfer between LNAPL and GW?

**Commented [DE8]:** Suthersand et al. (2011) gives 2000 mg/l for sulfate no longer rate limiting

Based on the model and its output, study topics for the first phase of sulfate reduction at the site include:

1. Will engineered degradation rates yield attainment of remedial objectives in desired timeframes?
2. Will the sulfate reducing bacteria (SRB) biomass grow as needed?
3. What is the optimal concentration for sulfate injection?
4. Will highly concentrated injections of sulfate be inhibitive to bacterial activity?
5. Will the injected sulfate become well distributed with respect to NAPL accumulations?
6. What is the lag time for SRB to acclimate to elevated sulfate concentrations (not included in the model)?
7. Inhibition by other degradation processes and nutrient availability are not included in the model, are these factors important?
8. Will hydrogen sulfide concentrations or other reaction products inhibit degradation or will subsurface conditions mitigate their buildup?
9. If/when sulfate is no longer limiting rates of degradation, what will limit the reaction and what degradation rates can be expected?
10. Is benzene slower to degrade than other aromatics, or faster, or average?
11. Will periodic sulfate injections or recirculation be necessary to sustain degradation rates?
12. How will the actual depletion of aromatic compounds from NAPL be assessed?

**Commented [DE9]:** State a predictive model must be developed to determine this?

**Commented [WU10]:** Eleanor's microbial analyses could help here, but it's a complex question because the SRBs need a whole consortia to be able to work well. But if we see large increases in SRBs in response to increases in GW sulfate, that is at least encouraging in terms of potential success of EBR.

**Commented [WU11]:** How would we determine what an optimal concentration might be?  
There might possibly be an optimal concentration of sulfate in terms of sulfate concentration in action (in contact with microbes and COCs) in the subsurface, but the injection concentration is a complex dance around desired final sulfate concentrations in the subsurface, distribution of sulfate from injection points, injection rates, number/location of injections points, injection frequency, LNAPL distribution, and etc.

**Commented [WU12]:** Probably, but it would be impossible to avoid some degree of inhibition with any reasonable injection scheme, I think. But AF appears to have ...

**Commented [WU13]:** Unlikely, unless they do a lot of injection points, and injection/extraction to move the injectate around. All the years of P&T and SEE and ...

**Commented [WU14]:** Probably going to be difficult to practically address this question. We might need to be prepared ...

**Commented [WU15]:** Nutrient availability is important, but usually addressed through just incorporating "plenty of" nutrients in the reagent injectate, rather than studying ...

**Commented [WU16]:** Probably slower, but the literature is all over the map on this.

**Commented [WU17]:** I think they've backed off the massive sulfate injections – by reducing the concentrations, and increasin ...

**Commented [WU18]:** Key factor. If they claim to be able to use EBR to deplete LNAPL of COCs (and this depletion is a major part of the success of the remedy), ...

**Commented [DE19]:** ?